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Readily Applicable Method for Caffeine Detection in Surface Waters by Optimized Solid-Phase Extraction and Capillary Gas Chromatography-Mass Spectrometry

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INTRODUCTION

- Caffeine can be used as a chemical marker in water quality studies to improve the accuracy in detecting sources of domestic wastewater pollution[1-3]. This application, however, is still limited by the lack of standardized and validated analytical methods for caffeine that can be readily implemented in environmental laboratories, such as a GC/MS-based method.
- Critical to sufficient sensitivity of the analytical method is the efficiency of the extraction procedure. The preferred method for sample preparation and pre-concentration is solid-phase extraction (SPE). In order to maximize sensitivity, the SPE procedure needs to be optimized for caffeine extraction. The selectivity of an extraction sorbent for caffeine is determined by the polarity of analyte and sorbent, and whether specific molecular interactions occur.
- The optimized analytical method for caffeine requires evaluation of its performance in terms of accuracy, precision, sensitivity, and applicability to the analysis of real-world surface water samples.

OBJECTIVES

- Adapt a commonly used U.S. EPA analytical method for semi-volatile organic compounds in drinking water (Method 525.2) for the analysis of caffeine in surface waters.
- Optimize the SPE procedure by evaluating the extraction efficiency and capacity of various types of extraction sorbents for caffeine.
- Determine overall method detection limit (MDL) for the best-performing SPE sorbents, and validate the method using fortified matrix samples from marine and river waters.
- Apply the optimized method in microbial/fecal source-tracking studies to demonstrate its utility to expand the use of caffeine as a chemical marker.

METHODOLOGY

- Water samples (1 L) were extracted using one of the following pre-cleaned and conditioned Empore extraction disks (3M) (47-mm diameter):
  - octacdecyl (C-18)
  - styrene-divinylbenzene cross-linked (SDB-XC)
  - styrene-divinylbenzene reversed-phase sulfonated (SDB-RPS)
- The C-18 disks were eluted with ethyl acetate (EtAc), methylene chloride ($MeCl_2$), and 1:1 (v/v) EtAc/$MeCl_2$. The SDB-XC and the SDB-RPS disks were eluted with acetone, EtAc, and 1:1 (v/v) EtAc/$MeCl_2$.
- Concentrated eluates (1 mL) and standards were analyzed by GC-MS (electron impact ionization and full scan setting) using $^{13}C_3$-caffeine as internal standard.

REFERENCES

1. Buerge, I. J.;et. al.; Caffeine, an anthropogenic marker for wastewater contamination of surface water. *Environ. Sci. Technol.* **2003;** *37*(4); 691-700.
2. Glassmeyer, S. T.; et. al.; Transport of chemical and microbial compounds from known wastewater discharges: Potential for use of indicators of human fecal contamination. *Environ. Sci. Technol.* **2005**; *39*, 5157-5169
3. Peeler, K. A.; et. al.; Tracking anthropogenic inputs using caffeine, indicator bacteria, and nutrients in rural freshwater and urban marine systems. *Environ. Sci. Technol.* **2006**; *40,* 7616-7622.

EXPERIMENTAL DATA

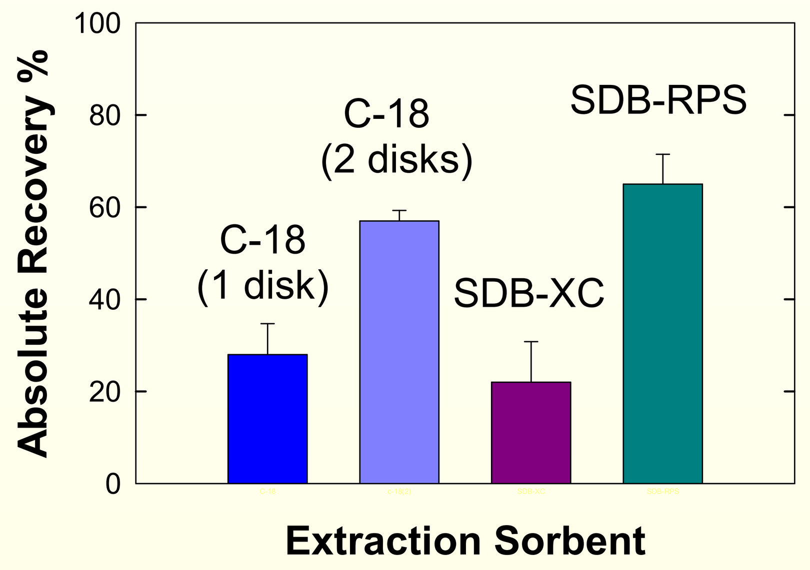


Fig. 1. Extraction efficiency of the various sorbents, expressed as absolute recovery percentage. (n = 3, spike level was 0.132 µg/L)

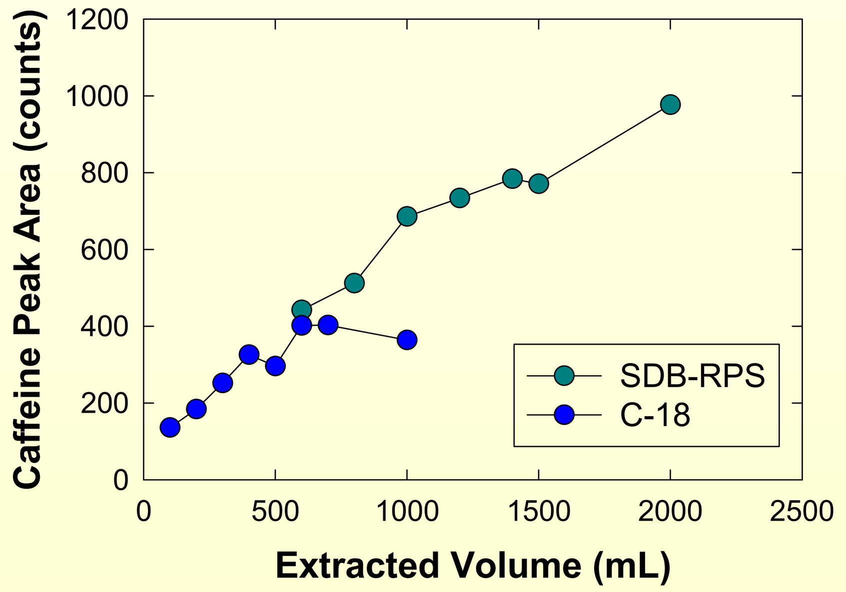


Fig. 3. Capacity of the disks for caffeine in laboratory fortified samples spiked at 0.132 µg/L.

Table 1. ***A***. Precision, accuracy, and method detection limit (MDL) determined from 7 laboratory fortified blanks over a 1-2 month time period. ***B***. Method validation data showing the recovery of caffeine in laboratory fortified matrix samples from surface waters in Massachusetts. (n=2)

A: MDL Data in Fortified Blanks	Disk Type	Recovery %	RSD %	MDL (µg/L)
LFB (0.132 µg/L)	C-18	100	6	0.027
LFB (0.065 µg/L)	SDB-RPS	99	7	0.016
B: Validation Data in Surface Water Samples				
Shawsheen River, Tewksbury, MA	C-18	100	11	
	SDB-RPS	104	5	
Savin Hill Cove, Boston Harbor, MA	C-18	104	1	
	SDB-RPS	97	1	
Merrimack River, Lawrence, MA	SDB-RPS	114	1	

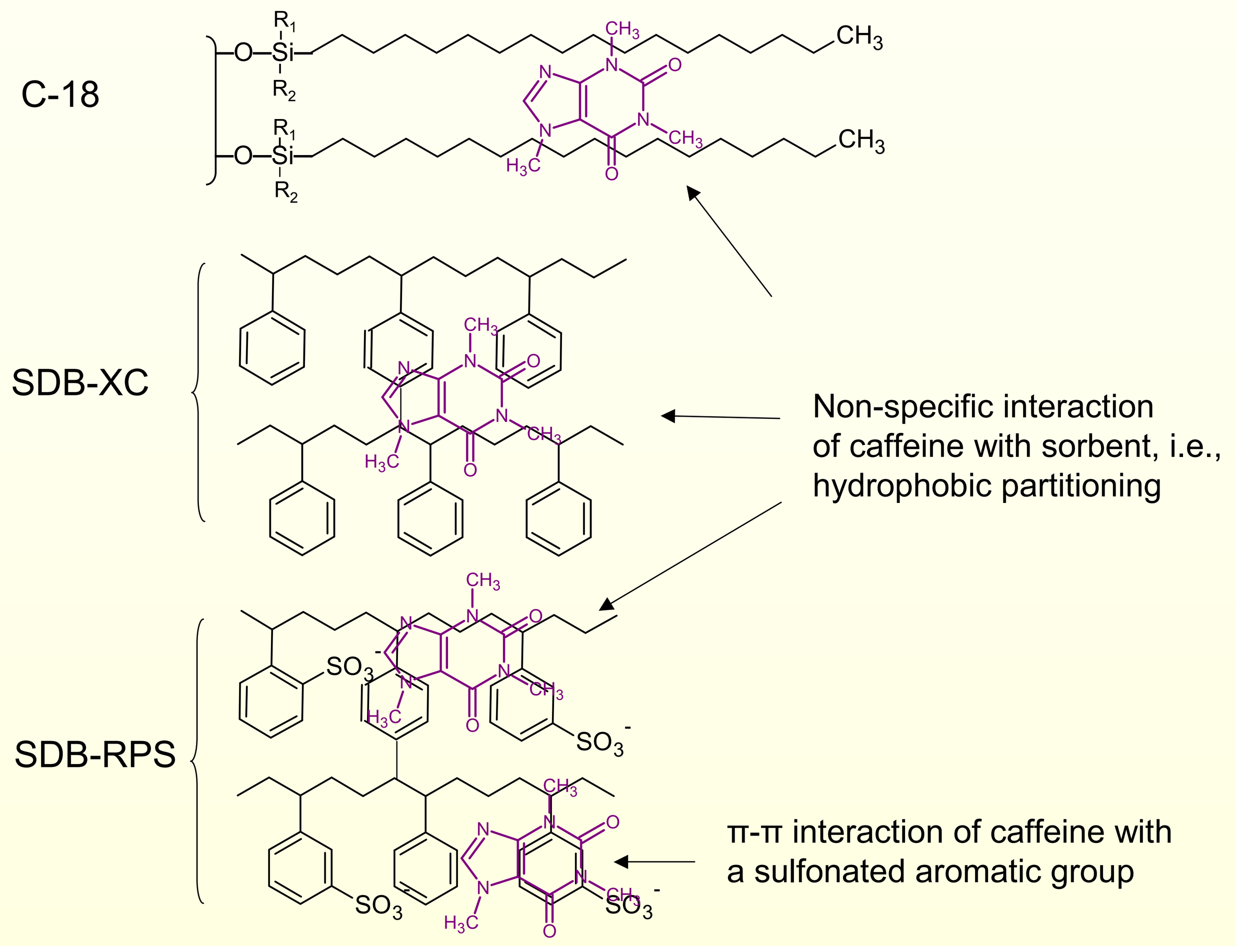


Fig. 2. The structures of the various extraction sorbents and an illustration of their modes of interaction with caffeine.

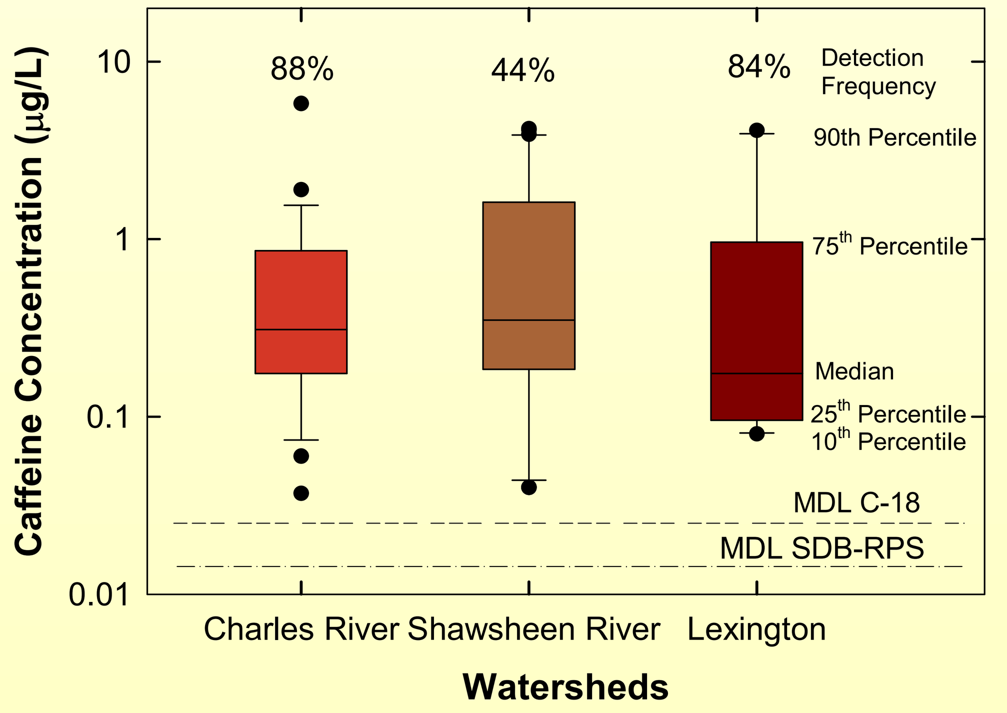
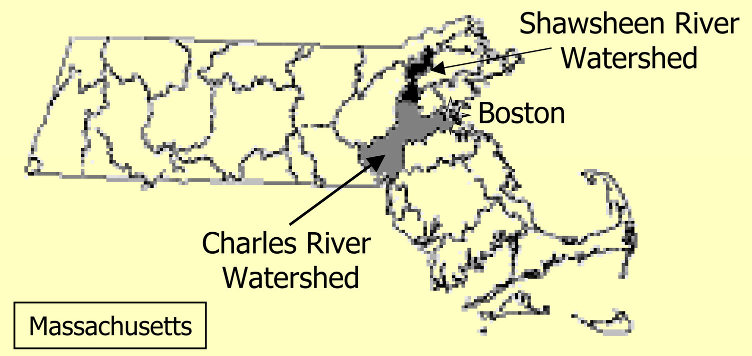


Fig. 4. Distribution of caffeine concentrations and detection frequency (i.e., >MDL) in samples taken from various rivers in Eastern Massachusetts during 2006. For the locations of the watersheds, see map below.



RESULTS & DISCUSSION

- The extraction efficiency data in **Fig. 1** show a relatively low efficiency of 28% for the general purpose C-18 disk. This sorbent is relatively non-polar and therefore has a low affinity for the relatively polar caffeine (log K_{ow} = -0.07). Two stacked C-18 disks increased the efficiency, but the highest efficiency (65%) was achieved with a single SDB-RPS disk.
- The sulfonation of aromatic groups appears to give the SDB-RPS sorbent a much higher affinity for caffeine compared to the unsubstituted SDB-XC sorbent (**Fig. 2**). The higher affinity of SDB-RPS is attributed to a better contact with the aqueous solution due to its hydrophilic character. In addition, the sulfonated groups may generate favorable π-π interactions between caffeine and the more π-electron accepting character of the sulfonated aromatic groups in this sorbent (**Fig. 2**).
- The capacity for caffeine retention of the SDB-RPS disk is much higher than the C-18 disk (**Fig. 3**). While the C-18 disk reached a maximum at 600 mL, the SDB-RPS disk did not reach a maximum even at an extracted volume of 2 L. Clearly, the SDB-RPS disk allows sufficient breakthrough volume to prevent substantial analyte loss in the typical 1-L sample volume.
- The data for the method detection limit (MDL) in **Table 1A** indicate a good accuracy and precision of this method. The SDB-RPS disk improves the method sensitivity considerably.
- The method validation data in **Table 1B** show acceptable recoveries in various river and marine water samples.
- The method was applied in support of several microbial/fecal source-tracking studies in watersheds with no permitted discharges in Massachusetts (see map): (*1*) The eastern highly urbanized section of the Charles River (34 samples, C-18 disks); (*2*) The suburban Shawsheen River (82 samples, C-18 disks); and (*3*) A selected area of the Shawsheen watershed near Lexington (13 samples, SDB-RPS disks). The distributions of the caffeine data from these three studies are shown as box-plots in **Fig. 4**. These data show that, when detected, the caffeine concentrations in these samples were frequently well above the MDLs of this method.

CONCLUSIONS

- Extraction using the C-18 sorbent shows reasonable performance, but superior sensitivity is achieved with the SDB-RPS sorbent, which has a higher affinity for caffeine due to its hydrophilic character and the possibility of π-π interactions between caffeine and the sorbent.
- Method detection limits and other validation data, and application data in source-tracking studies indicate a robust and accurate method for detecting caffeine in surface waters.
- This method, using readily available extraction setup and GC-MS instrumentation, offers expanded opportunities for the use of caffeine as a chemical marker of domestic wastewater in microbial/fecal source-tracking studies.

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